

Smith and the staff of the Adolph Basser Computing Laboratory, University of Sydney, for performing some of the calculations, and for the use of the IBM 650 computer of the Computation and Data Processing Center, University of Pittsburgh, and the structure-factor programme of R. Shiono (1957), for other calculations.

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*Acta Cryst.* (1961). **14**, 480

## The Crystal Structure of Diazoaminobenzene Copper (I)

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(Received 22 July 1960)

Crystals of diazoaminobenzene copper(I) are monoclinic, space group  $C_{2h}^2(I2/a)$  with

$$a = 16.00, b = 5.61, c = 24.01 \text{ \AA}; \beta = 99^\circ 20'$$

The structure has been determined by standard X-ray diffraction methods and refined by least-squares analysis of the three-dimensional intensity data ( $R = 0.09$ ).

The crystal contains discrete, centrosymmetric, approximately planar, dimeric molecules in which pairs of diazoamino groups are linked through linearly coordinated copper atoms to form an eight-membered ring (N-Cu, 1.90, 1.94 \AA). The trans-annular Cu-Cu separation, 2.45 \AA, is unusually small.

### Introduction

Diazoaminobenzene copper (I),



hereinafter referred to as DAB.Cu(I), is one of a series of stable complexes formed between diazoaminobenzene and transition metals (Dwyer, 1941). Little direct evidence from which a convincing structure could be proposed for DAB.Cu(I) has hitherto been available, although Meunier & Rigot (1900), who first prepared the compound, Dwyer (1941), and recently Harris, Hoskins & Martin (1959), have suggested possible atomic arrangements. The present paper, which describes the determination of its crystal structure, forms part of a wider study of compounds

containing copper(I) and azo groups (Brown & Dunitz, 1960).

### Crystal data

Diazoaminobenzene copper(I),  $C_{12}H_{10}N_3Cu$ .  
Monoclinic,

$$a = 16.00 \pm 0.05, b = 5.61 \pm 0.05, c = 24.01 \pm 0.05 \text{ \AA}; \\ \beta = 99^\circ 20' \pm 11'.$$

Volume of unit cell = 2127 \AA<sup>3</sup>.  
Density (measured) = 1.65 \pm 0.03 g.cm.<sup>-3</sup>.  
Density (calculated) = 1.62 \pm 0.03 g.cm.<sup>-3</sup>.  
Eight formula units per unit cell.  
Systematic absences:  $hkl$  if  $h+k+l$  is odd,  
 $h0l$  if  $h$  or  $l$  is odd.

Space group:  $C_s^4(Ia)$  or  $C_{2h}^6(I2/a)$ . The analysis leads to a structure based on the latter, centrosymmetric, space group which is conventionally described in terms of the orientation  $C2/c$ .

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Absorption coefficient for Cu  $K\alpha$  radiation =  $29.4 \text{ cm.}^{-1}$ .

### Experimental

DAB.Cu(I), prepared by the action of cuprous chloride on diazoaminobenzene (Meunier, 1900), is insoluble in water and most common organic solvents, but can be dissolved with difficulty in benzene. Crystals suitable for X-ray analysis, measuring approximately  $1 \text{ mm.} \times 0.2 \text{ mm.} \times 0.05 \text{ mm.}$ , were grown from a mixture of benzene and petroleum ether. Their density was measured by flotation in a mixture of bromoform and chloroform. Cell dimensions were determined from oscillation photographs about the three principal axes and from a Weissenberg photograph of the  $h0l$  net. NaCl powder ( $a_0 = 5.640 \text{ \AA}$ ) was used to calibrate the camera. Copper  $K\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ) was used throughout the analysis.

Visual intensity measurements were made with the aid of a calibrated intensity scale on multiple-film, equi-inclination, Weissenberg photographs of the five layers  $h0l$  to  $h4l$ . The intensities were multiplied by the usual Lorentz-polarization factor and brought to a common scale by interlayer comparisons on equi-inclination oscillation photographs, and, subsequently, by measurements made with the single-crystal counter diffractometer designed by Arndt & Phillips (1957). No corrections were made for absorption. Rough values for the absolute scale and temperature factors were obtained by Wilson's (1942) method. Out of the 950 non-equivalent reflexions which were examined, 612 were recorded with measurable intensity.

### Structure analysis

Approximate coordinates for all the atoms (except hydrogen) were obtained from the three-dimensional

Table 1. *Final atomic coordinates and standard deviations*

Atom	$x/a$	$y/b$	$z/c$	$\sigma$ ( $\text{\AA}$ )	$B$
Cu	0.0097	0.0844	0.0477	0.004	3.30
N <sub>1</sub>	0.0788	0.3169	0.0200	0.017	2.71
N <sub>2</sub>	0.0991	0.3290	-0.0291		3.11
N <sub>3</sub>	0.0673	0.1618	-0.0648		2.62
C <sub>11</sub>	0.1194	0.5130	0.0559	0.025	3.41
C <sub>12</sub>	0.1642	0.6944	0.0343		3.81
C <sub>13</sub>	0.1992	0.8826	0.0702		4.44
C <sub>14</sub>	0.1894	0.8824	0.1268		3.86
C <sub>15</sub>	0.1418	0.7019	0.1473		3.66
C <sub>16</sub>	0.1051	0.5085	0.1121		3.94
C <sub>21</sub>	0.0884	0.1897	-0.1185	0.025	3.32
C <sub>22</sub>	0.0600	0.0169	-0.1588		3.79
C <sub>23</sub>	0.0741	0.0288	-0.2156		5.08
C <sub>24</sub>	0.1240	0.2156	-0.2299		4.16
C <sub>25</sub>	0.1560	0.3852	-0.1901		4.13
C <sub>26</sub>	0.1369	0.3782	-0.1340		4.54

The numbering of the atoms corresponds to that used in Fig. 2. All the coordinates, temperature factors ( $B$ ) and standard deviations are based on the final round of least-squares analysis.

Patterson function computed with unmodified  $F^2$  values. The  $x$  and  $z$  coordinates were then refined by six successive difference syntheses based on the  $h0l$  data alone. This reduced the reliability factor  $R$  ( $\Sigma|F_o - F_c|/\Sigma|F_o|$ ) for this zone from 0.25 to 0.12 (observed reflexions only).

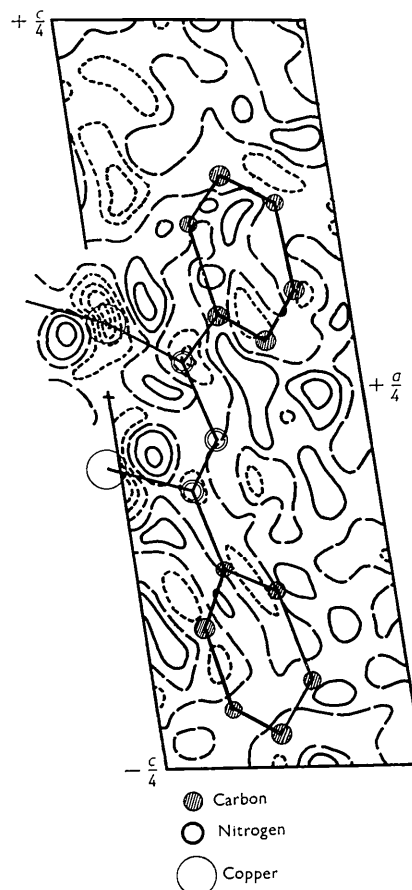


Fig. 1. The final difference synthesis based on the  $h0l$  structure factors given in Table 3. Contours are drawn at  $\frac{1}{2} \text{ e.}\text{\AA}^{-2}$ , positive contours are shown with a full line, negative contours with a dotted line and the zero contour with a broken line.

The  $x$ ,  $y$ , and  $z$  coordinates and  $B$ , the isotropic temperature factor, for each atom were then refined by six successive cycles of diagonal least-squares analysis of the complete three-dimensional data. Equal weight was given to all reflexions, and unobserved reflexions were treated as  $\Delta F = F_{\text{min.}} - F_c$  for  $F_c > F_{\text{min.}}$  and as  $\Delta F = 0$  for  $F_c \leq F_{\text{min.}}$ . The atomic scattering factors of Berghuis *et al.* (1955) were used; Cu values were corrected for dispersion (Dauben & Templeton, 1955). The least-squares refinement reduced  $R$  from 0.16 to 0.09 and  $\Sigma(F_o - F_c)^2/\Sigma(F_o)^2$  from 0.042 to 0.014. Since the shifts indicated by the final cycle are considerably less than the corresponding standard deviations, little advantage would be derived from further refinement.

Table 2. *Interatomic distances and angles*

Intramolecular distances and angles			
Between	Distance	$\sigma$	Mean value
Cu-Cu'	2.451 Å	0.008 Å	2.451 Å
Cu-N <sub>1</sub>	1.898	0.018	1.92 ± 0.02
Cu'-N <sub>3</sub>	1.939		
N <sub>1</sub> -N <sub>2</sub>	1.274	0.029	1.30 ± 0.03
N <sub>2</sub> -N <sub>3</sub>	1.316		
N <sub>1</sub> -C <sub>11</sub>	1.48	0.03	1.44 ± 0.04
N <sub>3</sub> -C <sub>21</sub>	1.39		
C <sub>11</sub> -C <sub>12</sub>	1.39	0.04	1.40 ± 0.02
C <sub>12</sub> -C <sub>13</sub>	1.42		
C <sub>13</sub> -C <sub>14</sub>	1.39		
C <sub>14</sub> -C <sub>15</sub>	1.40		
C <sub>15</sub> -C <sub>16</sub>	1.44		
C <sub>16</sub> -C <sub>11</sub>	1.40		
C <sub>21</sub> -C <sub>22</sub>	1.39		
C <sub>22</sub> -C <sub>23</sub>	1.42		
C <sub>23</sub> -C <sub>24</sub>	1.39		
C <sub>24</sub> -C <sub>25</sub>	1.39		
C <sub>25</sub> -C <sub>26</sub>	1.43	0.04	
C <sub>26</sub> -C <sub>21</sub>	1.40		
C <sub>16</sub> -C <sub>22</sub>	4.23	0.04	
C <sub>11</sub> -C <sub>21</sub>	4.52		
C <sub>12</sub> -C <sub>26</sub>	4.37		
Angles at copper			
	Angle	$\sigma$	Mean value
Cu'-Cu-N <sub>1</sub>	86.0°	1.0°	86.1 ± 0.1°
Cu'-Cu-N <sub>3</sub>	86.2		
N <sub>1</sub> -Cu-N <sub>3</sub>	171.8	1.0	171.8
Angles at nitrogen			
Cu-N <sub>1</sub> -C <sub>11</sub>	122.1	2.0	122.2 ± 0.1
Cu'-N <sub>3</sub> -C <sub>21</sub>	122.2		
Cu-N <sub>1</sub> -N <sub>2</sub>	127.6	2.0	125.9 ± 1.7
Cu'-N <sub>3</sub> -N <sub>2</sub>	124.2		
C <sub>11</sub> -N <sub>1</sub> -N <sub>2</sub>	110.2	2.0	111.8 ± 1.6
C <sub>21</sub> -N <sub>3</sub> -N <sub>2</sub>	113.4		
N <sub>1</sub> -N <sub>2</sub> -N <sub>3</sub>	115.8		115.8
Angles at carbon			
N <sub>1</sub> -C <sub>11</sub> -C <sub>12</sub>	122.0	3.0	123.0 ± 1.0
N <sub>3</sub> -C <sub>21</sub> -C <sub>26</sub>	124.0		
N <sub>1</sub> -C <sub>11</sub> -C <sub>16</sub>	114.9	3.0	116.3 ± 1.4
N <sub>3</sub> -C <sub>21</sub> -C <sub>22</sub>	117.7		
C <sub>11</sub> -C <sub>12</sub> -C <sub>13</sub>	119.6	3.0	120.0 ± 2.1
C <sub>12</sub> -C <sub>13</sub> -C <sub>14</sub>	119.7		
C <sub>13</sub> -C <sub>14</sub> -C <sub>15</sub>	119.7		
C <sub>14</sub> -C <sub>15</sub> -C <sub>16</sub>	122.0		
C <sub>15</sub> -C <sub>16</sub> -C <sub>11</sub>	115.8		
C <sub>16</sub> -C <sub>11</sub> -C <sub>12</sub>	123.0		
C <sub>21</sub> -C <sub>22</sub> -C <sub>23</sub>	123.4		
C <sub>22</sub> -C <sub>23</sub> -C <sub>24</sub>	117.4		
C <sub>23</sub> -C <sub>24</sub> -C <sub>25</sub>	120.6		
C <sub>24</sub> -C <sub>25</sub> -C <sub>26</sub>	121.3		
C <sub>25</sub> -C <sub>26</sub> -C <sub>21</sub>	119.0		
C <sub>26</sub> -C <sub>21</sub> -C <sub>22</sub>	118.3		

Table 2 (cont.)

Intermolecular distances		
Contacts between parallel molecules related by <i>b</i> translation		
Between	Distance	
Mean planes	3.23 Å	
C <sub>13</sub> -Cu(010)	3.20	
N <sub>1</sub> -N <sub>1</sub> '(010)	3.27	
C <sub>16</sub> -N <sub>3</sub> '(010)	3.36	
C <sub>12</sub> -Cu(010)	3.36	
N <sub>1</sub> -N <sub>2</sub> '(010)	3.51	
C <sub>11</sub> -N <sub>3</sub> '(010)	3.54	
C <sub>16</sub> -C <sub>21</sub> '(010)	3.55	
C <sub>11</sub> -N <sub>2</sub> '(010)	3.56	
C <sub>15</sub> -C <sub>22</sub> '(010)	3.64	
C <sub>15</sub> -C <sub>21</sub> (010)	3.69	
Contacts between molecules related by glide planes		
Between	Distance	
C <sub>12</sub> -C <sub>12</sub> '( <i>a</i> )	3.42 Å	
C <sub>15</sub> -C <sub>24</sub> ( <i>c</i> )	3.81	
C <sub>23</sub> -C <sub>23</sub> ( <i>c</i> )	3.87	
C <sub>25</sub> -C <sub>14</sub> ( <i>a</i> )	3.87	
C <sub>25</sub> (010)-C <sub>11</sub> '( <i>a</i> )	3.89	
C <sub>26</sub> (010)-C <sub>14</sub> ( <i>a</i> )	3.92	
C <sub>26</sub> -C <sub>14</sub> ( <i>a</i> )	3.95	
C <sub>26</sub> (010)-C <sub>13</sub> '( <i>a</i> )	3.96	
C <sub>26</sub> -C <sub>13</sub> ( <i>a</i> )	3.99	

The numbering of atoms is that used in Table 1. Atoms related by inversion through the origin are primed ('), those related by *a* and *c* glide planes are indicated by (*a*) and (*c*) respectively, while others are indicated by the appropriate lattice translation thus: (010). In each case the inversion operation is assumed to precede the translation operation.

The final parameters, together with the standard deviations derived from the least-squares analysis, are given in Table 1.

A final difference synthesis based on these parameters is reproduced in Fig. 1. The hydrogen atoms, which were neglected throughout the analysis, are not apparent. The thermal anisotropy, which is especially evident for the copper atom, may be an artifact attributable to our neglect of absorption errors.

Interatomic distances and angles, based on the coordinates of Table 1, are given in Table 2, together with the standard deviations.

### Description of the structure

DAB.Cu(I) exists in the solid state in the form of centrosymmetric dimeric molecules (Fig. 2) in which the diazoaminobenzene units (in all *trans* configuration) are linked by nearly linear N-Cu-N coordination to form an eight-membered ring. To a first approximation the molecule can be described as planar (see Table 4), with point symmetry *mmm*. The two Cu-N distances, 1.898 and 1.939 Å (both ± 0.018 Å), do not differ significantly, nor do the N-N distances, 1.274 and 1.316 Å (both ± 0.029 Å). The difference between the two C-N distances, 1.48 and 1.39 Å (both ± 0.03 Å), is possibly significant. The bond lengths and angles found in the phenyl groups do not differ significantly from the accepted values of 1.39 Å and 120° respectively.

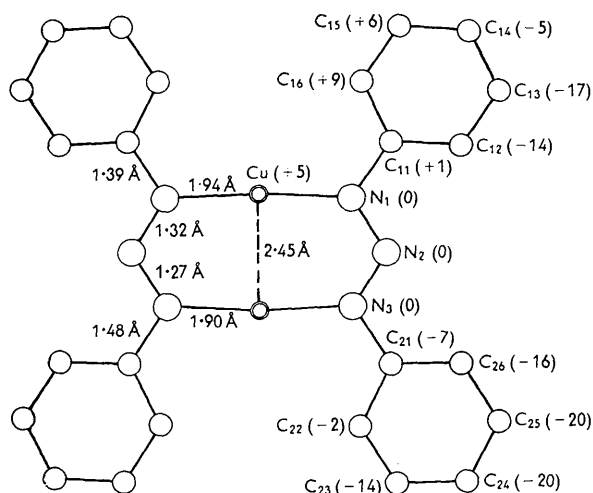


Fig. 2. The structure of DAB.Cu(I) in the molecular plane. The numbering of the atoms corresponds to that used in Table 1. The number in parentheses by each atom indicates its deviation, expressed in units of  $10^{-2}$  Å, from the plane of the nitrogen atoms.

### Discussion

In a recent paper, Harris, Hoskins & Martin (1959) have discussed the stereochemistry of the transition-metal diazoaminobenzene complexes. Our work establishes the correctness of one of the two models which they propose for DAB.Cu(I).

The results are not sufficiently accurate to permit us to draw conclusions concerning bond orders, but the observed distances and angles are quite compatible with an electronic structure in which each nitrogen atom has a single electron in a  $\pi$ -orbital normal to the molecular plane and a pair of electrons in an  $sp^2$   $\sigma$ -orbital in the molecular plane. The  $\pi$ -orbitals of the nitrogen atoms are, of course, delocalised and must also interact to some extent with the  $\pi$ -orbital systems of the adjacent phenyl groups and with the empty  $4p$ - $\pi$  orbitals of the Cu(I) atoms. The additional electron per diazoaminobenzene anion would then be in such a delocalized  $\pi$ -orbital extending perhaps over the entire molecule. The unshared pairs of electrons on the two terminal nitrogen atoms point in the direction of the copper atoms, as in the cuprous chloride:azomethane complex (Brown & Dunitz, 1960). In both cases a dative  $\sigma$ -bond is formed with electron transfer from N to  $Cu^+$ . The mean N-Cu distance in the DAB.Cu(I) dimer,  $1.92 \pm 0.03$  Å, appears to be shorter than the corresponding distance,  $1.99 \pm 0.02$  Å, in the cuprous chloride:azomethane complex, and this may be ascribed to the greater anionoid properties of the unshared pairs in the negatively charged diazoaminobenzene ion compared with those of the neutral azomethane molecule, or, if preferred, to the decrease in the coordination number of the copper from 4 to 2.

The coordination around the copper atom shows a number of interesting features. DAB.Cu(I) is one of the few compounds in which Cu(I) is known to occur in linear coordination (see also  $Cu_2O$ , Bragg & Bragg (1915);  $CuFeO_2$ , Soller & Thompson (1935);  $CuCrO_2$ , Dannhauser & Vaughan (1955)). But in addition to its two linearly coordinated nitrogen atoms, the copper atom possesses a third close neighbour; the Cu-Cu distance across the centre of symmetry is only  $2.45 \pm 0.02$  Å, shorter than that,  $2.56$  Å, in metallic copper and that,  $2.64 \pm 0.03$  Å, in the weakly paramagnetic cupric acetate complex (Niekerk & Schoening, 1953) where a Cu-Cu bonding interaction is known to occur. In the present case, where the shortness of the Cu-Cu separation is a consequence of the overall molecular geometry, there seems no reason to invoke any special type of bonding between the copper atoms. Indeed, for perfectly linear N-Cu-N coordination, the Cu-Cu distance would be the same as that between the nitrogen atoms  $N_1$  and  $N_3$ ,  $2.19$  Å, considerably less than the observed separation. The increase to  $2.45$  Å is associated with a deviation of the N-Cu-N system by about  $8^\circ$  from linearity. In addition to the distortion in the mean molecular plane, which can be seen in Fig. 2, there is also a small out-of-plane component, the Cu atoms lying  $0.05$  Å on opposite sides of the plane of the nitrogen atoms.

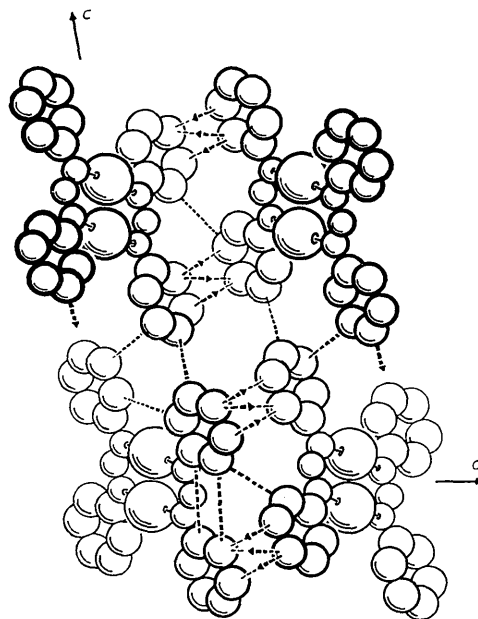


Fig. 3. The arrangement of the dimers viewed down the  $b$  axis showing the contacts between molecules related by the glide planes.

The required crystallographic symmetry of the molecule is  $\bar{1}$ , but, as has been mentioned, the molecule approximates quite closely to  $mmm$  symmetry. The particular system of the six nitrogen atoms is



Table 4. *Equations of the best planes through the dimer and through the individual rings*

Expressed in the form  $ax' + by' + cz' + d = 0$  where  $x' = x + z \cos \beta$ ;  $y' = y$ ;  $z' = z \sin \beta$ ;  $x$ ,  $y$ , and  $z$  in Å

Plane	$a$	$b$	$c$	$d$
A. Whole molecule	+0.7705	-0.5698	+0.2856	0
B. Central ring (N atoms only)	+0.7535	-0.5814	+0.3067	0
C. Phenyl group I (C <sub>11</sub> -C <sub>16</sub> )	+0.8110	-0.5296	+0.2485	-0.1652
D. Phenyl group II (C <sub>21</sub> -C <sub>26</sub> )	+0.7948	-0.5431	+0.2705	-0.1602

Angles between planes			
	$B$	$C$	$D$
$A$	1.9°	3.9°	2.4°
$B$	—	5.6	3.9
$C$	—	—	1.9

Deviations of atoms from these planes				
	$A$	$B$	$C$	$D$
Cu	+0.029 Å	+0.048 Å		
N <sub>1</sub>	+0.034	+0.003	-0.030 Å	
N <sub>2</sub>	+0.060	-0.004		
N <sub>3</sub>	+0.068	+0.003		-0.012 Å
C <sub>11</sub>	+0.042	+0.008	+0.013	
C <sub>12</sub>	-0.066	-0.137	-0.004	
C <sub>13</sub>	-0.101	-0.173	-0.011	
C <sub>14</sub>	-0.008	-0.045	+0.017	
C <sub>15</sub>	+0.059	+0.058	-0.008	
C <sub>16</sub>	+0.092	+0.094	+0.006	
C <sub>21</sub>	+0.037	-0.066		-0.007
C <sub>22</sub>	+0.088	-0.020		+0.025
C <sub>23</sub>	+0.009	-0.135		-0.020
C <sub>24</sub>	-0.026	-0.204		-0.002
C <sub>25</sub>	-0.024	-0.199		+0.020
C <sub>26</sub>	-0.026	-0.164		-0.016

planes of adjacent molecules is 3.23 Å. The columns are related to each other by the crystallographic glide planes as is shown in Fig. 3. Each molecule forms 70 van der Waals contacts with its neighbours: forty of these occur between parallel molecules within the columns, while the remainder are formed through the hydrogen atoms of the phenyl groups to molecules in neighbouring columns. In the former case, the contact distances, given in Table 2, are seen to lie between

3.2 and 3.7 Å whilst in the latter, because of the hydrogen atoms of the phenyl groups, the distances between carbon atoms are found for the most part in the range 3.8 to 4.0 Å. Since the carbon-carbon distances between different phenyl groups within the same molecule are all greater than 4.2 Å, there is no tendency towards overcrowding within the molecule. The temperature factors, listed in Table 1, indicate that the atoms at the perimeter of the molecule possess a larger amplitude of vibration than those at the centre.

We wish to thank Drs U. W. Arndt and D. C. Phillips for the use of their single crystal diffractometer, and Dr P. Pauling and Mr O. S. Mills for assistance in computing. The work described in this paper has been accepted by the University of London in part fulfillment of the requirements for the degree of Doctor of Philosophy conferred upon one of us (I. D. B.) who wishes, in addition, to thank the Department of Scientific and Industrial Research for a maintenance grant.

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